

CHARACTERIZATION OF Pt/SnO₂ CATALYSTS FOR CO OXIDATION

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SUMMARY

We present in this report the results of surface characterization of 2% and 1% (w/w) Pt on SnO₂ catalysts which are being used in promoting the oxidation of CO in pulsed CO₂ lasers. The N₂ adsorption BET surface area for both catalysts is 6.9 m²/g. The CO chemisorbed area at 313K is 0.17 m²/g and 0.062 m²/g for the 2% and 1% catalysts respectively. Monitoring the reaction between CO and O₂ by the same technique, at the same temperature yields a turn-over frequency (TOF) for the 2% catalyst of 2.7×10^2 molecules of CO₂/site/s and for the 1% catalyst a value of 1.2×10^2 . The ratio of the TOFs for the two catalysts is 2.2 which is approximately the ratio of the Pt loading.

INTRODUCTION

The determination of the mechanism for the catalytic oxidation of CO requires the measurement of the number of CO molecules that are capable of being adsorbed by the catalyst. Initial attempts to measure the amount of CO adsorbed upon the oxide-supported Pt catalyst utilized the pulse technique first described in references 1-4. However, the initial measurements proved to be quite unreliable since the catalyst was capable of being reduced by the CO even at the moderate temperature (313K) where the measurement was performed. The detector was not able to discern between reactant CO and product CO₂ making it impossible to determine the amount of CO adsorbed. Any attempt to pursue these measurements at the higher temperatures where the catalyst would be expected to operate would also be fruitless.

The pulse technique was then modified to include, following the procedure described in reference 5 (developed to study the methanation of CO), a packed column after the catalyst to allow for the separation and analysis of the reactants and products. The amount of product produced and the amount of material left upon the surface could, then, be determined. This report is a summary of these measurements for the two catalysts currently being employed at NASA-Langley for the catalytic oxidation of CO, 1%Pt-SnO₂ and 2%Pt-SnO₂.

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EXPERIMENTAL

The experimental apparatus consists of a Shimadzu gas chromatograph with a "CTR" column obtained from Alltech which enables the quantitative separation of CO and CO₂. The catalyst is placed on a frit located prior to the column in the same containment area as the column. Approximately 0.1g of catalyst can be placed upon the frit. The exact weight for each catalyst sample is determined with an analytical balance having an accuracy of 0.1 mg. The catalyst and column are under He flow at all times with a flow rate of 40 sccm and a temperature of 313K. The detector is a thermal conductivity detector whose response for each gas is calibrated using standards of known concentration with Ne added as an internal standard. For CO adsorption the test gas is 5%CO in He obtained from Scott Specialty Gases. The injections onto the catalyst are performed using the 1 mL sample injection loop of the Gas Chromatograph. Each injection contained 2.05×10^{-6} moles of CO. We also performed chemisorption studies with gas mixtures that contained 1%CO and 0.5% O₂ in He. The injection size was also 1mL corresponding to 4.09×10^{-7} moles of CO and 2.05×10^{-7} moles of O₂ at each injection. The 1%- and 2%-Pt/SnO₂ catalysts were obtained from Englehard Industries as a catalog item. The method of synthesis is regarded as proprietary information. The Pt loading is a weight percent given by the manufacturer with no further attempt made to determine the precise Pt loading of the catalyst. Due to the current limitations of the experimental design, which placed the catalyst and the column in the same GC oven, the catalyst was not pretreated. All of the data reported herein is, then, for the catalyst on an as received basis.

The surface area of each catalyst was determined by the Brunauer-Emmett-Teller (BET) method using a commercial instrument manufactured by Quantachrome corporation. The catalyst was placed in a glass u-tube and immersed in liquid N₂. The total amount of N₂ gas absorbed at different partial pressures of N₂ in He was determined and the surface area was calculated. For both the 1%Pt/SnO₂ and the 2%Pt/SnO₂ catalysts the determined surface area, by N₂ adsorption was 6.9m²/g.

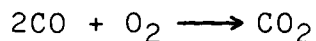
RESULTS AND DISCUSSION

The progress of the adsorption experiment with injections of 5% CO in He for both catalysts is summarized in figure 1. For both catalysts there is an initial production of CO₂ indicating that the surface is not in an entirely reduced state. The CO₂ production decreases rapidly reaching a low level after a few injections. The CO signal rapidly increases approaching the level that is observed with no catalyst present in the system. The injections were routinely performed at constant time intervals of 13 min. However, there were some breaks in the data since the

entire series of injections were done manually. The longest break in the data was for approximately 1.5 hrs. When the experiment was resumed, at the 20th injection for the 2% Pt-SnO₂ catalyst, the CO₂ production was found to have increased markedly with a concomitant decrease in the amount of CO detected. It would appear as if the surface of the catalyst had reoxidized during this period of time since the resultant behavior resembled that of the fresh catalyst. However, the catalyst was kept under a constant flow of pure Helium during the entire break period making reoxidation of the surface an unlikely event. Rather some sort of relaxation of the surface seems to have occurred producing surface sites that are capable of being reduced by the CO. This phenomenon of surface recovery is even more pronounced when the stoichiometric reaction mixture is run by the pulse technique as will be discussed below.

During the entire time period covered by the injections a small but significant amount of the injected CO is not detected as either CO or CO₂. It is assumed that the difference between the total number of moles of CO injected and that which appears at the detector as either CO or CO₂ is the number of moles of CO that is physisorbed or chemisorbed by the catalyst for each injection. The total number of moles of CO adsorbed can be expressed as a fraction of the total number of moles of Pt present in the catalyst, a quantity often referred to as the dispersion of the catalyst, in order to compare catalysts of differing amounts of added metal. The variation of the dispersion as the number of injections is increased is shown in figure 2. As might be expected the 1% Pt-SnO₂ catalyst levels off at a considerably lower value than that of the 2% Pt-SnO₂ catalyst. Indeed, the dispersion for the 2% catalyst has not leveled after 58 injections while the 1% catalyst appears to have leveled after thirty two injections. The dispersion is quite low for both catalysts attaining values of 1.2×10^{-2} and 1.8×10^{-2} for the 1% and the 2% catalysts respectively. If we assume that the adsorption is a monolayer and each CO is bound by one Pt atom then the amount of Pt at the surface that is capable of acting as an adsorption site for CO is only slightly greater than 1% of the total Pt present in both catalysts. The implication is that there is not a great deal of Pt present at the surface in either catalyst. The latter statement has been confirmed by recent ESCA measurements of this catalyst (G. Hoflund, University of Florida, private communication). If we further assume that the cross-sectional area of an adsorbed CO is $1.63 \times 10^{-19} \text{ m}^2$ (6) then the amount of surface area covered by the CO is 0.17 m²/g and 0.062 m²/g for the 2% and the 1% catalysts respectively. For the 2% catalyst the CO coverage is 2.5% of the N₂ BET surface area, for the 1% catalyst the percentage of BET area covered is 0.9%.

The progress of the catalyzed reaction between oxygen and carbon monoxide



may also be followed by the pulse technique. The results expressed in terms of percent loss of both O_2 and CO and the percent yield of CO_2 are shown in figure 3 for both the 1% and the 2% catalysts. Both catalysts are quite active initially with 2% catalyst removing approximately 90% of the CO and yielding almost 78% of the possible CO_2 . The activity of both catalysts declines rather rapidly tending to level off after 5 - 10 injections of the stoichiometric reaction mixture with neither catalyst exhibiting the pronounced minimum that is evidenced in the long term, continuous flow studies performed upon these catalysts at higher temperature range of 328 to 373K. Comparison of the yields after thirty injections shows that the 2% catalyst is approximately four times as efficient in terms of CO_2 yield as the 1% catalyst although the trend in yield for both catalysts is downward.

If we compare the amount of CO adsorbed on the Pt surface for both catalysts we observe a reversal of form when oxygen is present in the system. As is shown in figure 4 there is now more CO per mole of Pt adsorbed on the catalyst for the 1% catalyst than for the 2% catalyst. The difference is significant. In the case of the 2% catalyst the dispersion is approximately the same as that when the CO is added alone. For the 1% catalyst the dispersion is approximately ten times that which was determined when the CO was present in the gas mixture without oxygen.

An alternative way of comparing the two catalysts, which differ, chemically, only by the amount of Pt load, is to ratio the number of moles of product per second to the number of active sites available for reactant absorption. This ratio is referred to in the literature as the turn-over frequency (TOF) an effective normalization of catalyst reaction rate by a number which is characteristic of the catalyst surface. If we assume that the residence time is as calculated in reference 7 the TOF is 2.7×10^2 molecules of CO_2 /site/sec for the 2% catalyst and 1.2×10^2 molecules of CO_2 /site/sec for the 1% catalyst. The ratio of the TOF for the 2% catalyst to that of the 1% catalyst is 2.2, approximately equal to the Pt loading ratio. The maximum TOF is considerably lower than that reported in the literature on other oxide-supported catalysts. However, the temperature usually studied is 373K rather than the 313K performed here. If, as a rough approximation, we assume that the reaction rate doubles for every 10K rise in temperature the TOF at 373 for the 2% catalyst is 17.1×10^3 molecules of CO_2 /site/sec. This latter number compares quite favorably to the TOFs reported for Ru/SiO₂, Rh/SiO₂ and the Ru-Rh/SiO₂ reported in the literature at 373K with stoichiometric gas mixtures (8).

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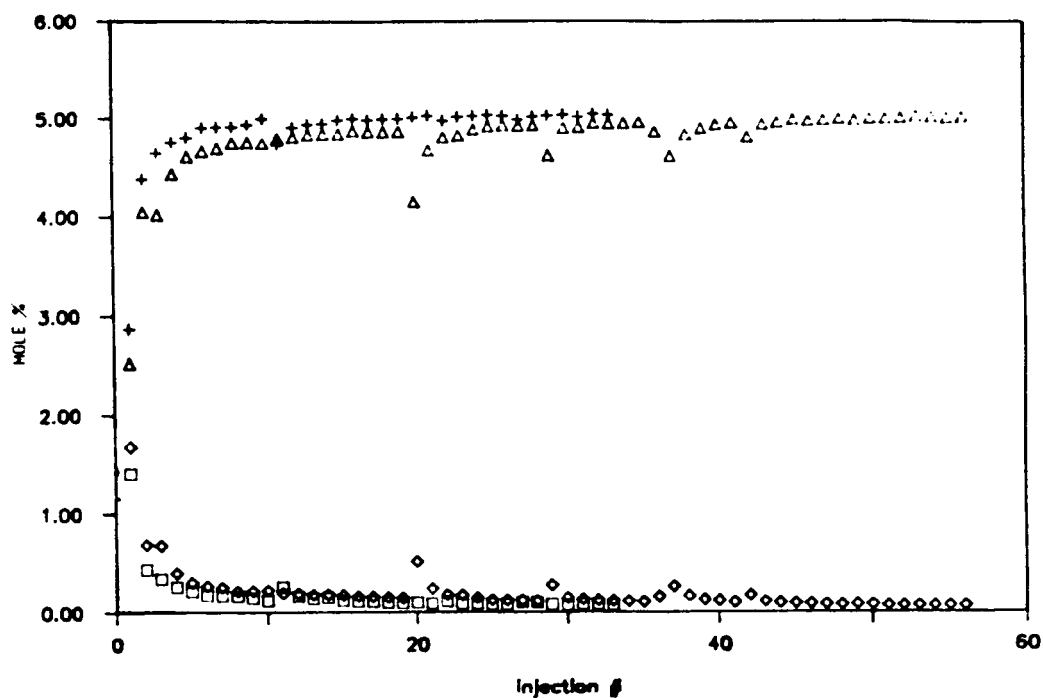


Figure 1: Fraction of Carbon Dioxide produced (lower) or Carbon Monoxide remaining (upper) for injections of 5% CO in Helium. +, \square 1% Pt/SnO₂, \diamond , \triangle 2% Pt/SnO₂

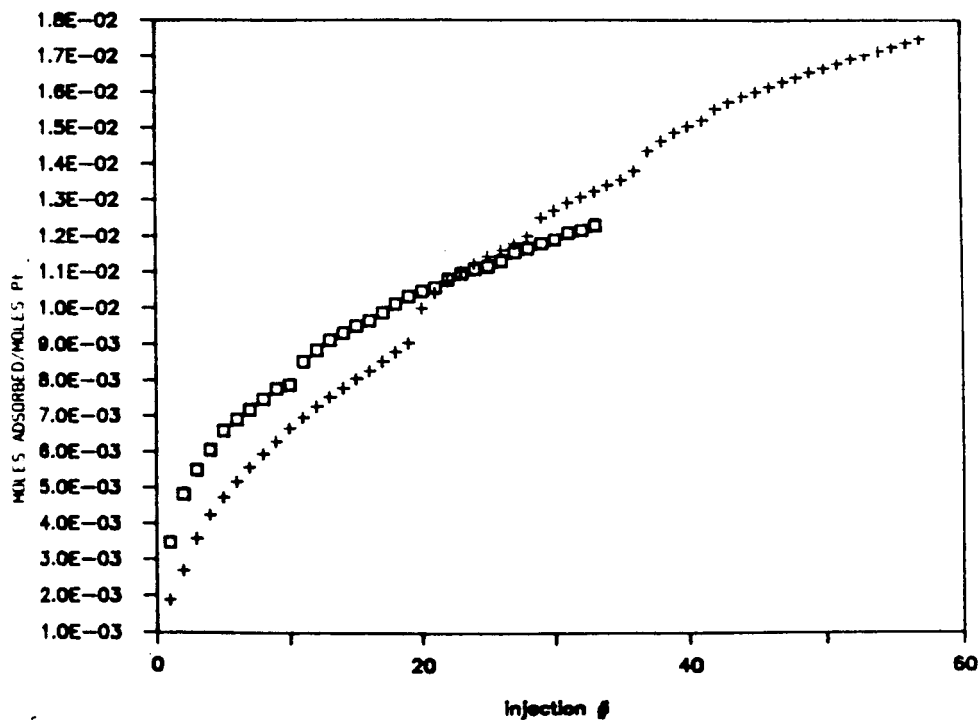


Figure 2: Dispersion as a function of injection for \square 1% Pt/SnO₂ and + 2% Pt/SnO₂

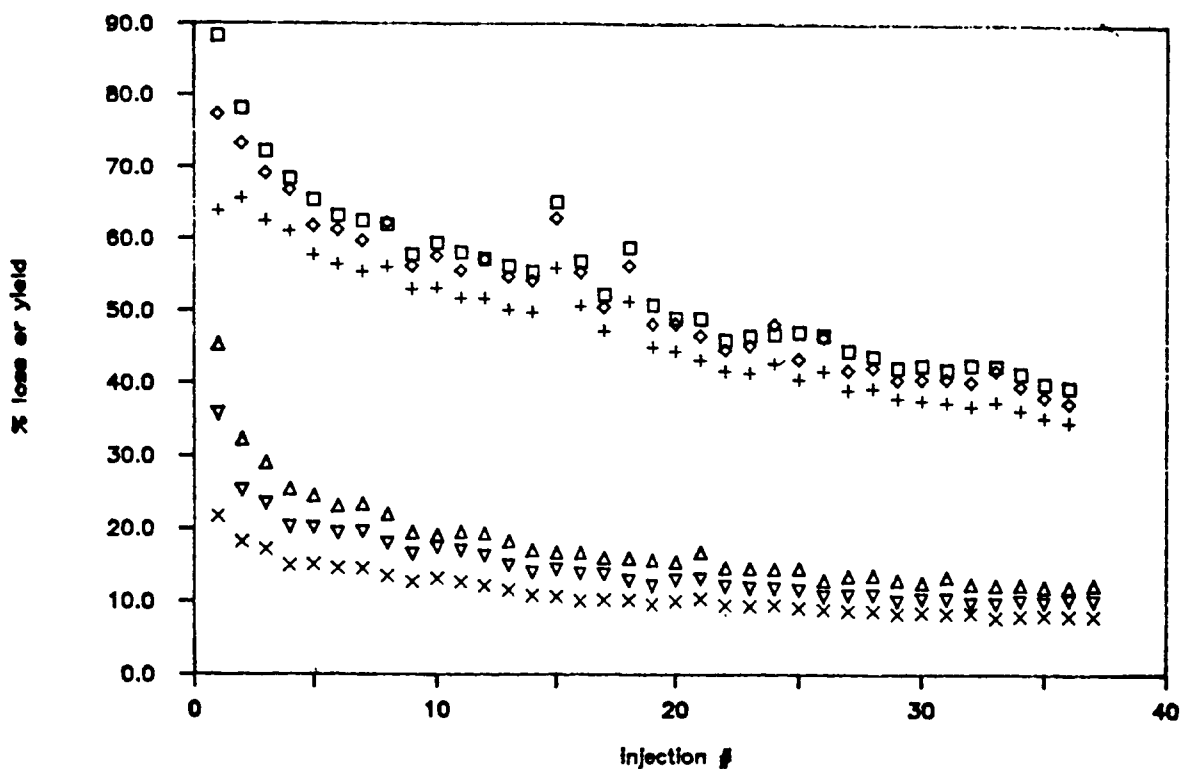


Figure 3: Chemisorption results for the injection of 1%CO, 0.5% O₂ in Helium upon 2% Pt/SnO₂(upper) and 1% Pt/SnO₂. \square , Δ loss of CO, \times loss of O₂, \diamond , \triangle yield of CO₂.

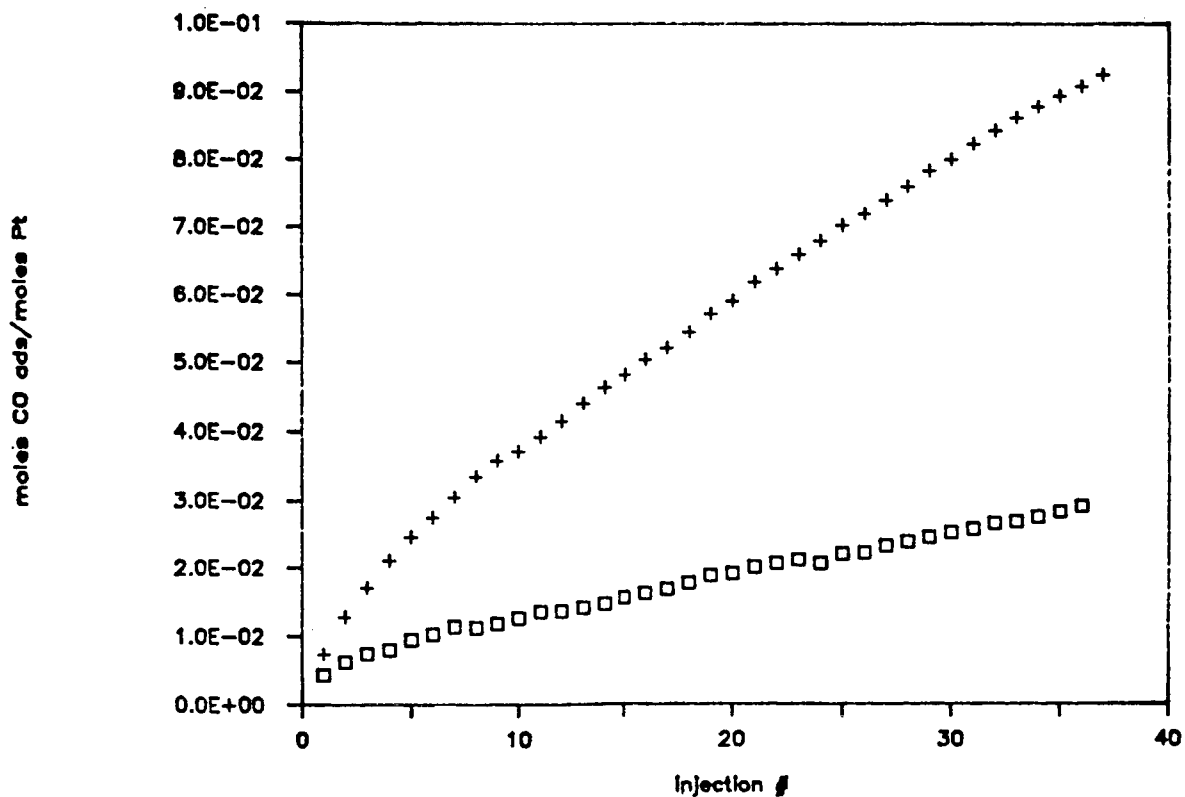


Figure 4: Total CO adsorbed per mole of Pt after each injection of the stoichiometric gas mixture. \square 2% Pt/SnO₂ + 1% Pt/SnO₂.